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STUDIES OF SILICON-NITROGEN-PHOSPHORUS COMPOUNDS INCLUDING A NE--ETC(U)  
AUG 81 R H NEILSON, P WISIAN-NEILSON

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| 19. KEY WORDS (Continue on reverse side if necessary and identify by block number)<br>poly(dialkylphosphazenes)<br>N-silylphosphinimines<br>silylaminophosphines<br>silicon-nitrogen-phosphorus<br>phosphazenes   |  |  |
| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br>This program of research has been directed toward the development of new synthesis of polyphosphazenes, particularly those with alkyl and/or aryl substituents, via the elimination of substituted silanes from N-silylphosphinimines. The synthesis and characterization of both the new polymers and their precursors has been investigated. |  |  |

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STUDIES OF SILICON-NITROGEN-PHOSPHORUS COMPOUNDS  
INCLUDING A NEW SYNTHESIS OF PHOSPHAZENES

Final Report

by

Robert H. Neilson and  
Patty Wisian-Neilson

August 11, 1981

U.S. ARMY RESEARCH OFFICE

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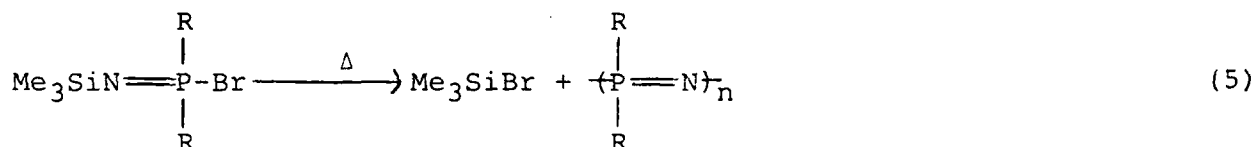
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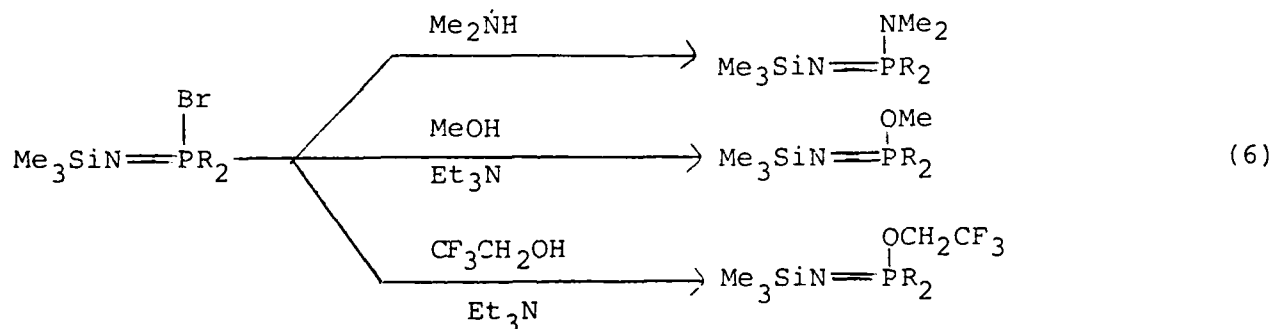
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An important, common feature of each of these oxidation reactions is subsequent cleavage of a Si-N bond as seen in the migration of Me<sub>3</sub>Si from nitrogen to oxygen in eq 2 and 4 and in the elimination of Me<sub>3</sub>SiBr in eq 3. Of particular importance is a similar Si-N bond cleavage upon thermolysis of the P-bromo, N-silylphosphinimine products in eq 3 to form exclusively cyclic phosphazenes (R<sub>2</sub>PN)<sub>n</sub> (n=3,4,5) (eq 5).

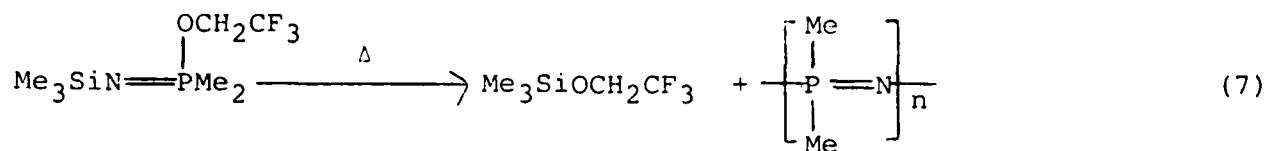


Since no evidence for polymer formation via Me<sub>3</sub>SiBr elimination was observed, the effect of changing the leaving group from Br to NMe<sub>2</sub>, OMe, and OCH<sub>2</sub>CF<sub>3</sub> was studied. The N-silylphosphinimine precursors were prepared from the P-bromophosphinimines (eq 6). Although



the NMe<sub>2</sub> and OMe derivatives were remarkably thermally stable, the OCH<sub>2</sub>CF<sub>3</sub> substituted phosphinimine readily eliminated Me<sub>3</sub>SiOCH<sub>2</sub>CF<sub>3</sub> to give quantitative yields of poly(dimethylphosphazene) (eq 7). Polymerization occurs on heating at 175 to 190°C in a sealed glass

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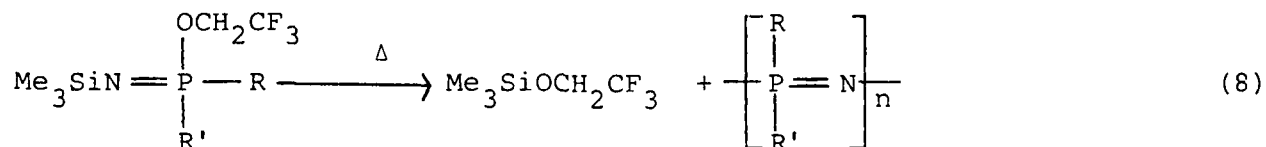


$$\bar{M}_w = 50,000$$

$$T_g = 42^\circ\text{C}, T_m = 158^\circ\text{C}$$

ampoule or in a stainless bomb, or in refluxing benzene, or under neat reflux. The phosphinimine also decomposes slowly on standing at room temperature for extended periods of time.

The process was extended to prepare a number of new alkyl and/or aryl substituted polymers (eq 8). In general, higher temperatures



|    |    |    |    |    |
|----|----|----|----|----|
| R  | Me | Et | Me | Et |
| R' | Me | Et | Ph | Ph |

were required to facilitate polymer formation. Some of the physical properties that have been determined by AMMRC for  $[\text{Ph}(\text{Me})\text{PN}]_n$  are  $T_g = 37^\circ\text{C}$ ,  $[\eta] = 0.396 \text{ dl/g}$ ,  $M_n = 53,900 \pm 1700 \text{ g/mole}$ . Data for  $[\text{Ph}(\text{Et})\text{PN}]_n$  have not been received and no data is available for  $(\text{Et}_2\text{PN})_n$  due to its insolubility. Thermolysis of  $\text{Ph}_2\text{P}(\text{OCH}_2\text{CF}_3)_2 = \text{NSiMe}_3$  at  $225^\circ$  for 10 days resulted in only trace amounts of polymer as well as cyclic trimer and tetramer and undecomposed starting material.

Copolymerization of mixtures of differently substituted phosphinimines was also investigated. Heating of equimolar amounts of  $\text{Ph}(\text{Et})\text{P}(\text{OCH}_2\text{CF}_3)_2 = \text{NSiMe}_3$  and  $\text{Et}_2\text{P}(\text{OCH}_2\text{CF}_3)_2 = \text{NSiMe}_3$  or  $\text{Ph}(\text{Me})\text{P}(\text{OCH}_2\text{CF}_3)_2 = \text{NSiMe}_3$  and  $\text{Me}_2\text{P}(\text{OCH}_2\text{CF}_3)_2 = \text{NSiMe}_3$  proceeded smoothly to give two new polymeric materials. Complete characterization of these compounds is in progress.

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